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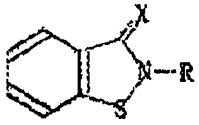
(54) [Title of the Invention] Industrial Fungicide

(57) [Summary]

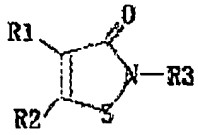
[Object] To provide an industrial fungicide for use in the alkaline range of papermaking processes or the like.

[Means of Achievement] An industrial fungicide, characterized by containing 1 to 100 parts by weight of a benzoisothiazolone derivative shown by general formula I, and 100 to 1 parts by weight of an isothiazolone derivative shown by general formula II as the active ingredients, and by being used in a pH range of 7 to 12.

[Chemical formula 1] General formula I



General formula II

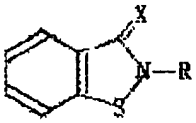


In general formula I, R is hydrogen or an alkyl group with 1 to 8 carbon atoms, and X is oxygen or sulfur. In general formula II, R1 and R2 are each a hydrogen or an alkyl group with 1 to 4 carbon atoms, and R3 is hydrogen, an alkyl group with 1 to 6 carbon atoms, or an alkoxy group with 1 to 4 carbon atoms. These may contain either or both alkali metals or amine-based compounds.

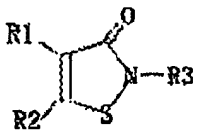
[Claims]

[Claim 1] An industrial fungicide, characterized by containing 1 to 99 parts by weight of a benzoisothiazolone derivative shown by general formula I, and 99 to 1 parts by weight of an isothiazolone derivative shown by general formula II as the active ingredients, and by being used in a pH range of 7 to 12.

[Chemical formula I] General formula I



General formula II



In general formula I, R is hydrogen or an alkyl group with 1 to 8 carbon atoms, and X is oxygen or sulfur. In general formula II, R1 and R2 are each a hydrogen or an alkyl group with 1 to 4 carbon atoms, and R3 is hydrogen, an alkyl group with 1 to 6 carbon atoms, or an alkoxy group with 1 to 4 carbon atoms.

[Claim 2] The industrial fungicide according to Claim 1, characterized by containing either or both an alkali metal and amine-based compound.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to an industrial fungicide for use in the alkaline range of papermaking processes or the like, or in alkaline environments such as fiber oiling agents, cutting oils, latexes, coating colors, lignins, starch slurries, starch pastes, paints, coking agents, and dye solutions.

[0002]

[Technological Background] Various industrial fungicides that use isothiazolone derivatives have been proposed in the past and put to practical use (refer, for example, to Japanese Kokoku Patent Nos. Sho 46-21240, Sho 60-54281, and Hei 7-37362).

[0003] However, even though 5-chloro-2-methyl-4-isothiazolin-3-one (abbreviated hereinafter as "C1-MIT") among the isothiazolone derivatives has an excellent fungicidal effect, it cannot be used by itself because it is extremely unstable in water. Means of making this compound more stable include using it as a mixture with 2-methyl-4-isothiazolin-3-one (abbreviated hereinafter as "H-MIT") (Kokoku Patent No. Hei 7-37362), and using the compound with metal complexes added.

[0004] C1-MIT also contains potentially environmentally-damaging chlorine, and either incurs a significant cost for treatment of the chlorine when disposed of after being used as a fungicide, or raises concerns about corrosion of structural members of the equipment by the chlorine that becomes dissociated for various reasons during use as a fungicide.

[0005] In contrast, H-MIT does not pose such problems of environmental damage or post-treatment and does not negatively affect structural members of the equipment during use, but it is not used alone because its fungicidal effect is less than that of C1-MIT. It is generally used as a mixture with C1-MIT as mentioned above.

[0006] Furthermore, H-MIT is present in the mixture in an H-MIT:C1-MIT ratio of about 1:9 to 3:9, so the amount of C1-MIT in this mixture is much greater (in other words, H-MIT is

currently used as a stabilizer for C1-MIT rather than as a fungicide). This makes it impossible to eliminate the aforementioned problems of C1-MIT.

[0007] Mixed fungicides composed of C1-MIT and H-MIT have an excellent fungicidal effect in the acidic to neutral range, but in the alkaline range, C1-MIT decomposes and loses its fungicidal efficacy, so the H-MIT that is stable in the alkaline range has a low content, and is hence incapable of producing a superior fungicidal effect.

[0008]

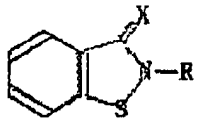
[Object of the Invention] An object of the present invention is to provide an industrial fungicide that is devoid of C1-MIT, which contains substances that cause environmental damage (chlorine), and that can exhibit an excellent fungicidal effect in the alkaline range.

[0009]

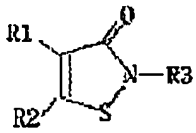
[Summary of the Invention] The industrial fungicide of the present invention is characterized by containing 1 to 99 parts by weight of a benzoisothiazolone derivative shown by general formula I, and 99 to 1 parts by weight of an isothiazolone derivative shown by general formula II as the active ingredients, and by being used in the pH range of 7 to 12. The industrial fungicide of the present invention that contains a benzoisothiazolone derivative shown by general formula I, and an isothiazolone derivative shown by general formula II in the above proportions as the active ingredients, may also contain either or both an alkali metal and amine-based compound.

[0010]

[Chemical formula 2] General formula I



General formula II



[0011] In general formula I, R is hydrogen or an alkyl group with 1 to 8 carbon atoms, and X is oxygen or sulfur. In general formula II, R1 and R2 are each a hydrogen or an alkyl group with 1 to 4 carbon atoms, and R3 is hydrogen, an alkyl group with 1 to 6 carbon atoms, or alkoxy group with 1 to 4 carbon atoms.

[0012] The joint use of a benzoisothiazolone derivative of general formula I, and an isothiazolone derivative of general formula II in accordance with the present invention has a synergistic effect brought about by these derivatives. In addition to improving stability in water and producing an excellent fungicidal effect without decomposition in the alkaline range, these derivatives are easier to dispose of after use in comparison with fungicides that contain Cl-MIT.

[0013] Specific examples of the benzoisothiazolone derivatives of general formula I (abbreviated hereinafter as "compound of general formula I") include 1,2-benzisothiazolin-3-thione, 2-methyl-1,2-benzisothiazolin-3-thione, 2-ethyl-1,2-benzisothiazolin-3-thione, 2-propyl-1,2-benzisothiazolin-3-one, 2-octyl-1,2-benzisothiazolin-3-one, 1,2-benzisothiazolin-3-one, 2-butyl-1,2-benzisothiazolin-3-one, and 2-methyl-1,2-benzisothiazolin-3-one.

[0014] Specific examples of the isothiazolone derivatives of general formula II (abbreviated hereinafter as "compound of general formula II") include 2-butyl-5-methyl-4-isothiazolin-3-one, 2-methoxy-4-isothiazolin-3-one, 5-ethyl-4-isothiazolin-3-one, 2-methyl-5-ethoxy-4-isothiazolin-3-one, 4,5-dimethoxy-4-isothiazolin-3-one, and 2-methyl-4-isothiazolin-3-one.

[0015] The compounds of general formulas I and II are combined together in a (compound of general formula I):(compound of general formula II) weight ratio of (1–99):(99–1), preferably (10–90):(90–10). If there is relatively too little of the compound of general formula I, the synergistic effect of the joint use of the compounds of general formulas I and II cannot be manifested. The desired fungicidal effect cannot be obtained if there is less than 1 part by weight of the compound of general formula I or more than 99 parts by weight of the compound of general formula II. Conversely, if there is relatively too much of the compound of general formula I, the synergistic effect of the joint use of the compounds of general formulas I and II cannot be achieved. The desired fungicidal effect cannot be obtained if there is more than 99 parts by weight of the compound of general formula I or less than 1 part by weight of the compound of general formula II.

[0016] The compounds of general formulas I and II are dissolved in a solvent in the aforementioned proportions and caused to form the fungicide of the present invention. The solvent is preferably one that does not interfere with the desired fungicidal effect when used in the alkaline range, and that allows simple disposal treatment to be performed. Specifically, the following can be used.

[0017] Water; glycols such as propylene glycol, triethylene glycol, and hexyl glycol; glycol ethers such as diethylene glycol, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, and diethylene glycol monoethyl ether; glycol diesters such as ethylene glycol diacetate; glycol ester ethers such as ethylene glycol monomethyl ether acetate and diethylene glycol monomethyl ether acetate; esters such as methyl acetate, ethyl acetate, 3-methoxybutyl acetate, 2-ethoxymethyl acetate, propylene carbonate, and dimethyl glutarate; amides such as dimethylformamide; ketones such as isophorone; pyrrolidones such as N-methyl-2-pyrrolidone; and the like. These may be used individually or in appropriate combinations of two or more types.

[0018] Glycol esters, glycol diesters, glycol ester ethers, esters, amides, ketones, and pyrrolidones among them may each be used individually, two or more types selected from among them may be used in combination, or these may be taken as the main components (specifically, 50% by volume or more) and used in combination with glycols as secondary components (specifically, less than 50% by volume).

[0019] The concentration of the active ingredients composed of the compounds of general formulas I and II in these solvents is about 1 to 80% by weight, preferably about 3 to 60% by weight, calculated as the total concentration of the compounds of general formulas I and II (i.e., concentrations of the active ingredients). If the concentration is too low, the fungicide of the present invention must be used in a greater amount, and the quality of the processes involved and the materials being treated may be adversely affected. Problems such as dissociation and precipitation of the active ingredient sometimes arise when the concentration is too high.

[0020] The fungicide of the present invention may contain alkali metals such as sodium or potassium, and amine-based compounds such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, diethanolamine, triethanolamine, diisopropanolamine, triisopropanolamine, morpholine, and diethylamine to

improve the storage stability of the compound of general formula I at 0°C or less and the stability and other properties of the compound of general formula I at higher concentrations, or to improve the solubility and dispersivity when using the fungicide of the present invention, particular a water-based one. These compounds may be used individually or in combinations of two or more types. A combination of an alkali metal and an amine-based compound may be used when two or more types are combined. It is especially preferable to use $H_2N(CH_2CH_2NH)_nH$ as the amine-based compound to attain the above-stated goals (to obtain various types of stability and to improve the solubility and dispersivity in a water-based system).

[0021] When the content of alkali metal or amine-based compound (the total quantity when an alkali metal and amine-based compound are used jointly) is too low, their presence has no technical significance. When the content is too high, their effect reaches saturation or the stability of the compound of general formula II instead declines. A quantity that ranges from an equimolar quantity (1.0 mol) to about 2 mol, and preferably from an equimolar quantity to 1.5 mol, in relation to general formula I is therefore appropriate.

[0022] The fungicide of the present invention can be prepared by adding active ingredients composed of the compounds of general formulas I and II to the aforementioned solvent and dissolving the compounds in the solvent. When an alkali metal or amine-based compound is to be added, it is possible to adopt a method in which the alkali metal or amine-based compound is dissolved by being added in advance to the aforementioned solvent, and the aforementioned active ingredients are then added to the resulting solution, or by a method in which the compound is added to and dissolved in the aforementioned solvent together with the active ingredients.

[0023] The fungicide of the present invention may be used in various ways, such as by adding the desired quantity beforehand to the process involved or the material to be treated, or by adding the desired quantity at the desired times. The process involved or the material to be treated may be in the neutral to acidic pH range, but the fungicide of the present invention can be used more effectively at pH 7 to 12, and preferably in the weakly alkaline to strongly alkaline range of pH 7.5 to 12.

[0024] The fungicide of the present invention is used effectively against microorganisms such as Bacillus, Pseudomonas, Micrococcus, and Flabobacterium that grow readily in the alkaline range. The amount in which the fungicide of the present invention is used cannot be determined unequivocally because this amount varies depending on the process involved or the material to be treated, and on the region and season of use. However, the process involved or the material to be treated should generally contain 0.00001 to 3%, preferably 0.000025 to 0.025%, of the active ingredients composed of the compounds of general formulas I and II.

[0025]

[Working Examples] Working Example 1

Fungicides 1 to 6 of the present invention and comparative fungicide 7 were first produced using the mixture ratios shown in Table 1 ("parts" means parts by weight)

[0026]

[Table 1]

(parts by weight)

1	1,2-Benzisothiazolin-3-one	20
	2-Butyl-5-methyl-4-isothiazolin-3-one	10
	Diethanolamine	10
	Sodium hydroxide	4
	Water	56
2	2-Butyl-1,2-benzisothiazolin-3-one	5
	2-Methyl-4-isothiazolin-3-one	20
	Triethanolamine	5
	Diethylene glycol monomethyl ether	50
	Water	20
3	1,2-Benzisothiazolin-3-thione	3
	2-Methyl-4-isothiazolin-3-one	27
	Diisopropanolamine	3
	Triethylene glycol	37
	Water	30
4	1,2-Benzisothiazolin-3-one	27
	2-Ethyl-4-isothiazolin-3-one	3
	Ethylene diamine	11
	Ethylene glycol monobutyl ether	15
	Water	44
5	2-Methyl-1,2-benzisothiazolin-3-one	20
	2-Methyl-4-isothiazolin-3-one	15
	N-methyl-pyrrolidone	50
	Water	15
6	1,2-Benzisothiazolin-3-one	15
	2-Methyl-4-isothiazolin-3-one	15
	Triethylene tetramine	28
	Diethylene glycol monomethyl ether	21
	Water	21
7	1,2-Benzisothiazolin-3-one	15
	5-Chloro-2-methyl-4-isothiazolin-3-one: 2-Methyl-4-isothiazolin-3-one = 10: 1 mixture	30
	Ethylene diamine	7
	Water	48

[0027] Next, the fungicides 1 to 7 shown in Table 1 were diluted with sterilized water and placed in laboratory dishes in concentrations of 1, 5, 10, 20, 30, 40, 50, 60, 70, 100, 330, 660, and 1000 ppm. Plate media were prepared by mixing bouillon agar medium that had been adjusted to pH 5, 7, 9, 10, and 12 in these dishes. These plate media were inoculated with pre-cultured microorganisms (*Pseudomonas aeruginosa*). After allowing the plates to stand for 48 hours at 33°C, the minimal inhibitory concentrations on the microorganisms were measured. The results are shown in Table 2.

[0028]

[Table 2]

Preparation No.	Test medium pH				
	Minimal inhibitory concentration (ppm)				
	5	7	9	10	12
1	60-70	60-70	60-70	60-70	50-60
2	20-30	20-30	20-30	20-30	20-30
3	10-20	10-20	10-20	10-20	10-20
4	60-70	60-70	60-70	60-70	60-70
5	30-40	30-40	30-40	30-40	30-40
6	40-50	40-50	40-50	30-40	30-40
7	100-330	100-330	330-660	>1000	>1000

[0029] As is evident from Table 2, the fungicides 1 to 6 of the present invention have an excellent fungicidal effect in the alkaline pH range of 9 to 12.

[0030] Working Example 2

One part by weight of rancid metal cutting oil was added as a source of test organisms to 99 parts by weight of metal cutting oil (made by Daido Kagaku Kogyo) that had been diluted 20-fold with boiling tap water. The product had a pH of 10. The fungicides 1 to 7 shown in Table 1 of Working Example 1 were added to this product in a concentration of 500 ppm and stored in a 30°C thermostat. The live cell counts were measured after 3, 7, and 21 days. The results are shown in Table 3.

[0031]

[Table 3]

Preparation No.	After 3 days	After 7 days	After 21 days
1	1.6×10^3	0	0
2	5.3×10	0	0
3	0	0	0
4	2.2×10^3	0	0
5	1.9×10^2	0	0
6	0	0	0
7	4.1×10^5	2.7×10^6	1.9×10^8
None added	2.8×10^6	3.4×10^7	2.2×10^8

[0032] As is evident from Table 3, the fungicides of the present invention 1 to 6 had an excellent fungicidal effect on strongly alkaline metal cutting oil of pH 10. This fungicidal effect was also judged to persist over a long period of time.

[0033] Working Example 3

One part by weight of spoiled starch-based coating solution for papermaking was added as a source of test organisms to 99 parts by weight of pH 10.2 starch-based coating solution for papermaking. The fungicides 1 to 7 shown in Table 1 of Working Example 1 were added to the solution in a concentration 350 ppm and stored in a 30°C thermostat. The live cell counts were measured after 3, 7, and 21 days. The results are shown in Table 4.

[0034]

[Table 4]

Preparation No.	After 3 days	After 7 days	After 21 days
1	1.1×10^3	1.2×10^3-	3.3×10
2	5.3×10^3	4.2×10	0
3	2.1×10^3	1.8×10^2	0
4	2.7×10^2	6.7×10	0
5	1.4×10^2	2.1×10^3	1.7×10^2
6	1.6×10^3	6.3×10	0
7	2.5×10^5	3.8×10^6	4.3×10^6
None added	4.6×10^5	2.8×10^7	5.7×10^6

[0035] As is evident from Table 4, the fungicides of the present invention 1 to 6 exhibited an excellent fungicidal effect on strongly alkaline starch-based coating solutions for papermaking with a pH of 10.2. Furthermore, this fungicidal effect was judged to persist for a relatively long period of time.

[0036]

[Effect of the Invention] As has been discussed in detail above, the industrial fungicide of the present invention is capable of having an excellent fungicidal effect in the weakly alkaline to strongly alkaline range of pH 7 to 12. Furthermore, this excellent fungicidal effect can persist for a long period of time. The industrial fungicide of the present invention is also gentle on the environment and therefore can be disposed of after use with relative ease.